Preface

Lithium ion conducting glasses are extremely important materials for technological applications since the small size light weight and highly electropositive character of lithium facilitate the use of these materials in solid state batteries and other electrochemical devices A large portion of studies on solid electrolytes has been devoted to lithium ion conducting glasses Although a large number of lithium ion conducting glass systems have been prepared and characterised there seems to be very little understanding of the mechanism of ion transport in these materials particularly in relation with the local structures In this thesis three different lithium ion conducting glass systems have been studied in detail with a view to understanding their structural aspects vis a vis their conduction behaviour Such a study is likely to be helpful for further development and design of glassy lithium ion conducting electrolytes

The thesis is divided into seven chapters Chapter 1 gives a broad overview of glassy state and glass transition (including the different models) criteria for glass formation and models to describe glass structure It also describes the different experimental techniques to study glass structure (with special emphasis on MAS NMR technique which has been used quite extensively in this thesis) along with the structure of phosphate and borate glasses This chapter also provides a brief review of the mechanisms of ionic conduction in glasses and the lithium ion conducting glass systems studied so far in the literature both of which have a direct bearing on the subject matter of the thesis

Chapter 2 describes the characterisation studies on a wide range of compositions in the ternary glass system Li_2SO_4 Li_2O P_2O_5 with an aim to understand the role of Li_2SO_4 in the structural modification of these glasses Molar volume variation thermal properties IR Raman and ^{31}P MAS NMR spectroscopies have been used

for this purpose Lithium phosphate glasses are made up of long chains/rings of phosphate tetrahedra in the metaphosphate compositions and shorter phosphate chains at higher levels of modification (high Li_2O content) The structure can be understood in terms of a random close packing of oxide ions When Li_2SO_4 is introduced the metaphosphate and sulphate ions are also in random close packing with structural voids which increase in proportion to the metaphosphate Voids have been visualised to be approximately of the size of oxide ions and can be seen as forming a percolating network Evidences from the variation of the thermal properties (glass transition temperature T_g and specific heat C_p) from vibrational spectroscopic features and from ^{31}P MAS NMR resonances indicate that phosphate and sulphate ions could be interacting weakly to form SPO_7^{3-} units (dithiophosphate species) The reasons for and the consequences thereof of the formation of such species have been discussed

Chapter 3 describes the structural role of Li_2SO_4 in highly modified lithium borate glasses A large number of compositions in the ternary glass system Li_2SO_4 Li_2O B_2O_3 have been prepared and characterised for this purpose Modification of B_2O_3 has been varied extensively so as to span compositions from metaborate (Li_2O/B_2O_3 =1) to pyroborate (Li_2O/B_2O_3 =2) Li_2SO_4 content has been varied from 0 40 mole / There are evidences for the retention of excess four coordinated boron (B_4) in these glasses from the variation of molar volume and thermal properties with composition as also from IR Raman and ^{11}B MAS NMR spectroscopies It has been suggested that retention of excess B_4 in these glasses is possible through an interaction among the metaborate and sulphate species resulting in the formation of borosulphate species Features in the Raman spectra in the region of 800 960 cm^{-1} have been assigned to such species

Chapter 4 is an attempt to understand the structural role of PbO in modified lithium borate glasses PbO is unique in its ability to act both as a glass former

and a modifier In Li_2O PbO B_2O_3 glasses it is likely that PbO is incorporated into the network as $[PbO_{4/2}]^{2-}$ and in the process regenerates three coordinated boron (B_3^0) and four coordinated boron (B_4^-) at the expense of two and one coordinated boron (B_2^- and B_1^{2-} respectively) IR and Raman spectroscopic features support this conjecture The N_4 values determined from ^{11}B MAS NMR indicate that the B_4/B_3 ratios are higher in these glasses compared to PbO free borates and is consistent with the suggestion that PbO is incorporated into the network Large increase in molar volumes with increase of PbO also supports this model

Chapter 5 presents the results of the conductivity measurements and dielectric relaxation studies of glasses in the ternary glass system Li_2SO_4 Li_2O P_2O_5 in the temperature range of 150K to 450K and frequency range of 10Hz 10MHz DC conductivities of these glasses reveal the presence of two different activation barriers one in the high temperature and the other in the low temperature regions This seems to suggest the presence of an ultramicroscopic cluster tissue texture in these glasses The activation barriers for lithium ion transport in the clustered regions of Li_2SO_4 and the semicontinuous lithium phosphate are likely to be higher than that in the amorphous tissue regions Variation of ac conductivity with frequency follows the Almond West type of expression with a single exponent of the frequency The frequency exponent s also shows two distinct regimes of variation it decreases rapidly (from values $\approx$ 1) with temperature in the low temperature regime followed by a nearly constant value of around 0 5 above 250K The dielectric data has been analysed using a modulus formalism and the KWW exponent β values have also been calculated from an analysis of dielectric relaxation data Variation of β with temperature shows a behaviour similar to that of s The change in the trends of both β and s occurs around the same temperature as the change in trends of dc conductivities This lends further credence to the possible existence of a cluster tissue texture in these glasses

Chapter 6 summarises the results of dc and ac conductivities as well as dielectric relaxation studies on glasses belonging to the ternary system Li_2SO_4 Li_2O B_2O_3 Conductivity measurements have been carried out over wide ranges of temperature and frequency (150K-450K 10Hz 10MHz) DC conductivities of these glasses seem to exhibit two activation barriers below and above 250K It has been suggested that the low barrier region at low temperatures corresponds to ionic migration in the amorphous tissue region while the high barrier regime at high temperatures corresponds to that in the clustered lithium sulphate and borate rich regions The glasses thus appear to possess a cluster tissue texture very much similar to that in the Li_2SO_4 Li_2O P_2O_5 glasses AC conductivity also can be fitted to an Almond West type of behaviour with a single exponent s Variation of s with temperature shows two different regimes a high of nearly 1 0 in the low temperature region and a nearly constant value of around 0 5 above 250K The value of β calculated from the dielectric relaxation peaks exhibits a similar variation as s All these features seem to be strongly pointing towards the existence of a cluster tissue texture in these glasses

Chapter 7 describes the results of the investigations on the conductivity behaviour of Li_2O PbO B_2O_3 glasses It has been suggested in chapter 4 that in these glasses PbO extends the network features by getting incorporated into the structural frame work However in spite of formation of a rather open structure as a consequence of this feature PbO is found to inhibit lithium ion conductivity in this ternary system It has been argued that this could be because of increased effective negative charge on the oxygens attached to Pb and also could be due to the presence of the lone pair on Pb both factors impede lithium ion motion in these glasses The glasses also exhibit unusual dielectric properties like the near invariance of β with temperature